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Diffuse-Reflectance Mid-infrared Spectral Properties of Soils under Alternative Crop Rotations in a Semi-arid Climate

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We carried out mid-infrared (mid-IR) spectral interpretation of soils 0–5 and 5–15 cm deep in selected alternative crop rotations (ACR) treatments and an adjacent native prairie soil. Ashing and spectral subtraction shows that absorbance at 3700–2850 and 1700–1550 cm⁻¹ indicates organic absorbance. Prairie soils, with their greater carbon (C) content, have different spectral properties from the cropped soils. Prairie soils have greater absorbance at the 2950–2870 cm⁻¹ and the 1230 cm⁻¹ CH bands. The soils from the different depths had different spectral properties, with the soils 0–5 cm deep having stronger absorbance at the 1055 cm⁻¹ carbohydrate band, at 1270–1460 cm⁻¹, and at the 1730 cm⁻¹ ester band. The soils 5–15 cm deep are characterized by greater absorbance at the clay band. Soil C and nitrogen (N) correlated negatively with the 3700 cm⁻¹ clay band and the 1830 cm⁻¹ quartz band and correlated positively with the 2920 cm⁻¹ because of aliphatic CH absorbance.

Keywords Crop rotation, infrared spectroscopy, soil carbon, wheat

Introduction

The soils of the central Great Plains sustain one of the most important wheat-based agroecosystems in the world. These soils in their native state were fertile and provided good crops after the pioneers broke sod. Wheat (*Triticum aestivum* L.)–fallow (WF) was adopted during the 20th century to avoid financial risk, because the fallow period allows for soil water recharge for the following wheat crop (Smika 1970). The WF, however, quickly reduced soil organic matter because of the lack of photosynthesis during the fallow phase. The virgin grasslands lost up to 38% of soil organic carbon (C) 25 years after cultivation (Bauer and Black 1981). After 60 years of WF, up to 62% of the soil organic C was lost near the surface in a Colorado site that was originally under rangeland (Bowman et al. 1999).

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While the detrimental effect of cultivating native prairie soil has been well documented, the replenishment of soil organic matter (SOM) by alternative agronomic managements is a very active area of research. No-till management may allow for the elimination of fallow periods because surface crop residue permits more precipitation storage in the soil profile, and the intercrop period allows for soil organic N mineralization (Smika 1983). Reducing fallow frequency has the potential to ameliorate soil organic carbon (SOC) losses near the surface by increasing the supply of crop residue to the soil (Peterson et al. 1998; Bowman et al. 1999; Mikha et al. 2006). The alternative crop rotations (ACR) study is an ongoing project that was started in 1990 to test how decreasing the fallow frequency in wheat-based no-till dryland rotations affects annualized crop yields and biomass, soil quality, profits, and water utilization (Anderson et al. 1999). A previous analysis of the ACR data, 7 years after the start of the experiment, showed that reducing fallow frequency can result in greater SOM at the top 5 cm due to increased and more continuous production of crop biomass (Bowman et al. 1999). A subsequent study, 14–15 years after the establishment of the research plots, found that cropping intensity increased soil microbial biomass and enzyme activities at 0–5 cm deep, and undisturbed grass sites had the greatest microbial biomass compared to the cropped soils (Acosta-Martinez, Mikha, and Vigil 2007). This same study also shows that more frequent cropping resulted in different soil microbial composition according to fatty acid profiling. Benjamin, Mikha, and Vigil (2008) observed that 15 years after the establishment of the ACR, permanent grass and wheat–corn–millet plots had increased SOC and macroaggregation relative to wheat–fallow.

The sustainability and profitability of dryland agriculture depends on multivariate interactions (i.e., biological, chemical, or soil physical properties) that affect soil quality and functioning. It is essential to understand not only how management affects SOC quantity but also SOC quality. It becomes especially important to know how the chemical composition of SOM relates to the stability of soil C in a C sequestration context and also how SOM quality affects nutrient availability and crop performance.

Diffuse-reflectance Fourier-transformed mid-infrared spectroscopy (mid-IR) can be used to ascertain the quality of soil organic matter via spectral interpretation. Mid-IR has recently been used to reliably quantify soil C content (McCarty and Reeves 2000; Reeves, McCarty, and Reeves 2001; McCarty et al. 2002). Besides measuring the total C, mid-IR spectra ($4000\text{--}400\text{ cm}^{-1}$) have information about many soil chemical traits such as clay, carbonates, protein, polysaccharides, aromatics, aliphatics, and OH/NH bonds (Nguyen, Janik, and Raupach 1991; Haberhauer and Gerzabek 1999; Baes and Bloom 1989; Janik et al. 2007). Soil quality indicators such as those provided by mid-IR can be used to compare how different agronomic treatments affect soil C and can be used to understand how to optimize the sustainability of dryland agriculture. Although previous studies evaluated the differences in organic C content in the ACR (Acosta-Martinez, Mikha, and Vigil 2007; Benjamin, Mikha, and Vigil 2008), no data have yet been published regarding changes in SOC quality.

We hypothesize that reducing fallow frequency will cause differences in soil C quality. This study compared the mid-IR spectral properties of native prairie and ACR research plots that included grass and several crop rotations after 15 years of establishment. Our objectives were to (1) use multivariate analysis to pinpoint the soil spectral characteristics of the different crop rotations and depths, (2) carry out spectral interpretation to shed light on the chemistry associated with the treatments and depths, (3) distinguish between soil organic absorbance and soil mineral absorbance, and (4) evaluate soil components such as clay, silica, protein, humic acid, and starch using mid-IR.

Materials and Methods

The study was carried out on the ACR plots near Akron, Colorado (40.15° N and 103.15° W, 1384 m elevation). This area is in the High Plains of the United States where winter wheat dominates dryland crop production. The plots receive approximately 420 mm precipitation annually, although 2000–2005 were drier than average, with 2002 receiving less than 240 mm for the whole year. The soil is mapped as a Weld silt loam (fine, smectitic, mesic Aridic Paleustolls). The sampling depths in this study span the Ap horizon (0–120 mm), which has a silt loam texture with approximately 22% clay, and part of a Bt1 horizon of silty clay loam texture with approximately 32% clay.

The ACR experiment started in 1990 to test WF against several more intense crop rotations. Details about experimental design, plot establishment, and initial yields can be found in Anderson et al. (1999), and information about planting dates, agronomics, and weed control can be found in Acosta Martinez, Mikha, and Vigil (2007) and Benjamin, Mikha, and Vigil (2008). The experimental design is a randomized complete block with three replicates per rotation treatment, where each phase of the rotation is present every year. The following rotation treatments were selected for this study: wheat–corn–fallow (WCF), wheat–corn–millet–fallow (WCMF), wheat–corn–millet–pea (WCMPea), wheat–corn–millet (WCM), wheat–fallow conventional till (WF-CT), wheat–fallow no till (WF-NT), undisturbed planted grass plots (grass) mostly of smooth brome (*Bromus inermis*), and undisturbed native pasture (prairie). The prairie, which is adjacent to the ACR experiment but not part of the randomized design, has a mixture of bluegrama (*Bouteloua gracilis*) and buffalograss (*Buchloa dactyloides*). Cropped plots received ammonium nitrate according to projected crop yield and soil tests, but the grass and prairie sites were never fertilized. All the crop rotations were under no-till management except the WF-CT, which was tilled with V-blade undercutters for weed control. Weeds were controlled in the no-till plots with atrazine and glyphosate. Soil pH ranged from 4.3–5.8 for 0- to 5-cm depths and 5.1–6.1 for 5- to 15-cm depths at the time of sampling (Acosta-Martinez, Mikha, and Vigil 2007).

Soil samples were obtained in March 2005, 15 years after the start of the ACR. Ten 2.54-cm diameter cores taken randomly from each replicate plot and depth (0–5 and 5–15 cm) and were composited to make each soil sample. The samples were sieved (5-mm mesh) and then stored at 4 °C.

Soil Analysis

Microbial biomass C and nitrogen (N) (MBC, MBN) were measured on fresh soil (15 g dry equivalent) using the fumigation–extraction method of Vance, Brookes, and Jenkinson (1987), detailed in Acosta-Martinez, Mikha, and Vigil (2007).

All soil samples were air dried, ground with a mortar and pestle, and then analyzed for total soil C and N with a LECO Elemental Analyzer (LECO Corporation, St. Joseph, Mich.). The dried and ground soils were also scanned neat (not ashed) in the mid-IR (4000 to 400 cm⁻¹) on a Digilab FTS 7000 Fourier transform spectrometer (Varian, Inc., Palo Alto, Calif.) fitted with a Pike AutoDIFF automated diffuse reflectance sampler (Pike Technologies, Madison, Wisc.). The FTS 7000 had a potassium bromide beam splitter and a Peltier-cooled deuterated triglycine sulfate detector. Potassium bromide was used as background. Data were acquired as pseudo-absorbance (log [1/reflectance]). Resolution was set at 4 cm⁻¹, with 64 co-added scans per spectrum.

Besides the soil samples, we also scanned authentic standards of bentonite clay, starch, humic acid, silica, and casein to show the spectral properties of important soil components.

The bentonite, casein, and starch standards were run neat, while the silica and humic acid standards were diluted to 5% in KBr before scanning.

Ashing Procedure

Additional soil samples obtained in 2004 from selected ACR plots were analyzed before and after ashing (550 °C, 3 h). This approach is helpful to determine the spectral traits caused by organic matter as opposed to absorbance arising from soil minerals (Cox et al. 2000, Sarkhot et al. 2007). GRAMS/AI 8.0 (Thermo Fisher, Woburn, Mass.) was used to carry out the spectral subtractions of ashed from intact soil spectra.

Statistics

We used the Proc GLM of SAS 9.2 (SAS Institute Inc., Cary, N.C.) to carry out analysis of variance (ANOVA), as well as mean separations by Duncan's multiple-range test. The sample set from 2005 was made up of 120 samples, which included the different crop rotations and depths. The prairie samples were not part of the ACR experiment so the prairie data were not included in the ANOVA and instead are used as an external reference. Spectral differences between the treatments and depths were resolved by principal components analysis (PCA) using PLS Plus/IQ GRAMS/AI 8.0 (Thermo Fisher, Woburn, Mass.). Spectra were mean centered and multiplicative scatter corrected prior to PCA. Component loadings were used to show the spectral bands responsible for the sample scores.

Results and Discussion

Analysis of Variance of the Analyte Data

The organic C content of the soil surface layer is very important for dryland agroecosystem function because it affects how effectively precipitation infiltrates and is stored. Soils often benefit from no-till because the soil surface tends to increase in SOC (Reicosky et al. 1995). Table 1 shows the mean values for the soil analytes in the 0- to 5-cm and the 5- to 15-cm depths. All variables, except C to N ratio and bulk density, had a significant depth main effect according to ANOVA, $P < 0.05$ (not shown). The 0- to 5-cm depth has 56% greater total C and 55% greater N content on a soil mass basis, as well as 51% greater MBC and more than twice the MBN content than the lower depth. Bulk density and C to N ratios were not different between depths.

Analysis of the surface soils, 15 years after ACR establishment, suggests that no-till with less frequent fallow results in a measurable improvement in soil quality. Table 2 shows the mean analyte values for the different cropping treatments for the 0- to 5-cm depth. All variables had a significant cropping treatment main effect according to ANOVA, $P < 0.05$ (not shown). Total soil N and C follow similar patterns, with the greatest values in the grass, followed by the more intense crop rotations, and with the WF treatments having the lowest value. The grass plots, however, have not reached the total C and N levels of the prairie soils, indicating that it will take a longer time for grass plots to reach their C sequestration potential. Our results suggest that the best alternative for rebuilding of soil C from long-term cultivation is to simply establish undisturbed grass plots. Note that the grass plots were harvested for biomass during the first few years, with little aboveground C return to the soil, which might have lessened the soil C content at the time of sampling.

Table 1
Means and standard error of the mean (SEM) from the two soil depths obtained from the alternative crop rotations experiment in 2005

Variable	0–5 cm deep		5–15 cm deep	
	Mean	SEM	Mean	SEM
Total N (g kg^{-1})	0.93	0.03	0.60	0.02
Total C (g kg^{-1})	10.26	0.32	6.59	0.14
C to N ratio	11.04	0.14	11.08	0.16
Bulk density (mg m^{-3})	1.48	0.02	1.49	0.01
Nitrogen (mg ha^{-1})	0.69	0.02	0.89	0.02
Carbon (mg ha^{-1})	7.54	0.22	9.79	0.21
MBC ($\mu\text{g kg}^{-1}$)	95.72	9.12	63.25	4.97
MBN ($\mu\text{g kg}^{-1}$)	40.00	3.10	19.31	1.83

Notes. The data are the averages from all the ACR crop rotation treatments. The Prairie data is not included. MBC is microbial biomass carbon, MBN is microbial biomass nitrogen; $n = 60$, except for MBC and MBN.

The WF treatments had statistically equal soil N values regardless of conventional or no-till, but the no-till treatment had significantly greater soil C than the conventional till at the 0- to 5-cm depth. This is not a trivial increase, amounting to 1.4 Mg C on a per ha basis (Table 2). This tendency was not observed at the 5- to 15-cm depth (Table 3). These results suggest that at this stage of the ACR experiment, we are beginning to observe the increase in topsoil SOC often attributed to no-till systems (Reicosky et al. 1995).

The soil C to N ratio is an indicator of the decomposability of SOM. Low C to N values are associated with less SOM stability and potential C loss from the system. The C to N ratio varied between the ACR treatments, with the lowest value on the WF-CT (Table 2). The grass treatment had a lower bulk density than the majority of the crop rotations (Table 2). Soil compaction can be problematic in these soils (Benjamin, Mikha, and Vigil 2008), and our data show that permanent grass can decrease soil bulk density compared to cropping. The NT and CT were statistically indistinguishable in the WF treatments, even though the NT had greater soil C. Bulk density was lowest in the prairie soil, and this is accompanied by high C and N contents. The MBC also trending greater in the grass relative to some of the crop rotation soils. Even though the MBN in the grass plots was up to 50% greater than in the WCMF, the difference was not statistically significant. The effects of crop rotation on microbial biomass were the most pronounced of all the soil analytes, underscoring that soil microbes are quickly and markedly sensitive to changes in agronomic management, more so than soil C and N. Similar patterns were found for enzyme activities and microbial diversity in these treatments (Acosta Martinez, Mikha, and Vigil 2007), which were significantly different between the crop rotations at both depths. The prairie soils had MBC values several times greater than the ACR crop rotations.

As with the shallow samples, the prairie soils have more total soil C, N, and microbial biomass than the cropped soils at the 5- to 15-cm depth (Table 3). Note that even at the 5- to 15-cm depth, the prairie soil has more soil C, N and microbial biomass per unit of weight than the 0- to 5-cm soils from the ACR cropped sites (Tables 2 and 3). Within the ACR sites, the grass plots had greater total soil N, greater MBN, and lower bulk density (Table 3), indicating that grass has the potential to increase soil quality even beyond the

Table 2
Mean values from the eight cropping treatments (0–5 cm deep) obtained from the alternative crop rotations experiment in 2005

Variable	WCF	WCMF	WCMPea	WCM	WF-CT	WF-NT	Grass	Prairie
Total N (g kg^{-1})	0.90bc	0.92abc	0.95abc	1.10ab	0.73c	0.80c	1.14a	1.95
Total C (g kg^{-1})	10.20ab	10.40ab	10.62ab	11.56ab	7.22c	9.44b	12.24a	20.08
C to N ratio	11.37ab	11.25ab	11.20ab	10.54bc	9.89c	11.72a	11.01ab	10.20
Bulk density (mg m^{-3})	1.42bc	1.48ab	1.50ab	1.52a	1.54a	1.47ab	1.38c	1.25
Nitrogen (mg ha^{-1})	0.64bc	0.67bc	0.71abc	0.85a	0.56c	0.59c	0.77ab	1.22
Carbon (mg ha^{-1})	7.20ab	7.59ab	7.89ab	8.85a	5.53c	6.90bc	8.35ab	12.55
MBC ($\mu\text{g kg}^{-1}$)	54.69b	98.24ab	120.61ab	78.05b	108.83ab	87.93ab	155.89a	514.99
MBN ($\mu\text{g kg}^{-1}$)	41.02a	34.51a	40.53a	41.05a	45.60a	35.58a	51.23a	94.02

Notes. MBC is microbial biomass carbon, MBN is microbial biomass nitrogen. Means within a row that do not share a lowercase letter are significantly different according to Duncan's multiple-range test ($P < 0.05$). Prairie samples are not part of the ACR experiment and are not included in the statistical comparison.

Table 3

Mean values from the eight cropping treatments (5–15 cm deep) obtained from the alternative crop rotations experiment in 2005

Variable	WCF	WCMF	WCMPea	WCM	WF-CT	WF-NT	Grass	Prairie
Total N (g kg ⁻¹)	0.61 ^{ab}	0.62 ^{ab}	0.60 ^{ab}	0.64 ^{ab}	0.55 ^{ab}	0.51 ^b	0.68 ^a	1.28
Total C (g kg ⁻¹)	6.53 ^a	6.77 ^a	6.41 ^a	6.79 ^a	6.39 ^a	6.12 ^a	7.52 ^a	12.36
C to N ratio	10.75 ^b	11.17 ^{ab}	10.80 ^b	10.72 ^b	11.52 ^{ab}	12.07 ^a	11.09 ^{ab}	9.62
Bulk density (mg m ⁻³)	1.48 ^{ab}	1.52 ^a	1.50 ^{ab}	1.54 ^a	1.41 ^{cd}	1.45 ^{bc}	1.38 ^d	1.36
Nitrogen (mg ha ⁻¹)	0.91 ^{ab}	0.93 ^{ab}	0.90 ^{ab}	0.99 ^a	0.78 ^{ab}	0.74 ^b	0.93 ^{ab}	1.74
Carbon (mg ha ⁻¹)	9.67 ^a	10.26 ^a	9.61 ^a	10.47 ^a	9.01 ^a	8.83 ^a	10.35 ^a	16.79
MBC (μg kg ⁻¹)	48.00 ^b	66.98 ^{ab}	66.13 ^{ab}	43.11 ^b	97.63 ^a	53.23 ^{ab}	94.32 ^a	230.95
MBN (μg kg ⁻¹)	15.48 ^{ab}	19.58 ^{ab}	13.87 ^b	22.62 ^{ab}	27.77 ^{ab}	15.52 ^{ab}	30.15 ^a	52.39

Notes. MBC is microbial biomass carbon, MBN is microbial biomass nitrogen. Means within a row that do not share a lowercase letter are significantly different according to Duncan's multiple-range test ($P < 0.05$). Prairie samples are not included in the statistical comparison.

surface layer. Table 3 shows that WF-CT and WF-NT have similar total C values, indicating that the decline in total C in the WF-CT at the 0- to 5-cm depth is not simply a redistribution of surface C to deeper soil through tillage.

Spectral Properties of Authentic Standards

Bentonite has a prominent peak at 3622 cm⁻¹ (Figure 1), which indicates hydroxyl stretching in clays or alumino-silicates (Nguyen, Janik, and Raupach 1991). This clay feature appears in soil spectra with relatively low interference and is present in the physically separated clay-sized fraction of corn belt soils (Calderón et al., 2011). The starch absorbs at the broad band around 3400 cm⁻¹ for OH stretching, which can also be observed in the soil light fraction, humic acid, as well as most lightweight material of plant origin (Haberhauer and Gerzabek 1999; Calderón et al., 2011). Starch, and to a lesser extent casein and humic acid, all absorb at 2870–2950 cm⁻¹ (Figure 1), a spectral region that indicates CH in methyl and methylene groups. These bands have been found to be high in soils rich in organic C and are present in humic acids as well (Janik et al. 2007). The silica spectrum shows absorbance at three peaks between 2000 and 1790, which are quartz overtone combination bands, and like the clay band occur in a region relatively free of interference (Nguyen, Janik, and Raupach 1991). The casein spectrum has two peaks at 1660 and 1550 cm⁻¹ that are due to amide I and II absorption, and these bands are important in soil organic C determinations (Janik et al. 2007; Sarkhot et al. 2007). Humic acid, which can contain N, can also absorb strongly in the 1650 cm⁻¹ region (Shirshova, Ghabbour, and Davies 2006). Absorbance at 1580 cm⁻¹ in the humic acid is due to aromatic C=C, and this band has been observed in the stable fraction of organic matter (Baes and Bloom 1989; Sarkhot et al. 2007). The 1384 peak observed in the humic acid is possibly a combination band of phenolic or COO stretching vibrations with CH₂ and CH₃ bands. Note, however, that humic acids vary in this region, and Shirshova, Ghabbour, and Davies (2006) did not report strong humic acid absorbance at 1384 cm⁻¹. Janik et al. (2007) showed that the spectra from agricultural soils form a broad peak between 1270 and 1460, a spectral region relevant for soil organic C prediction. Bentonite has prominent peaks at 1260 and 650 cm⁻¹. Silica has peaks at 1100, 800, 700, 520, 470, and 400 cm⁻¹ possibly due to Si–O stretching and bending or OH bending absorptions (Madejová 2003). Starch absorbs

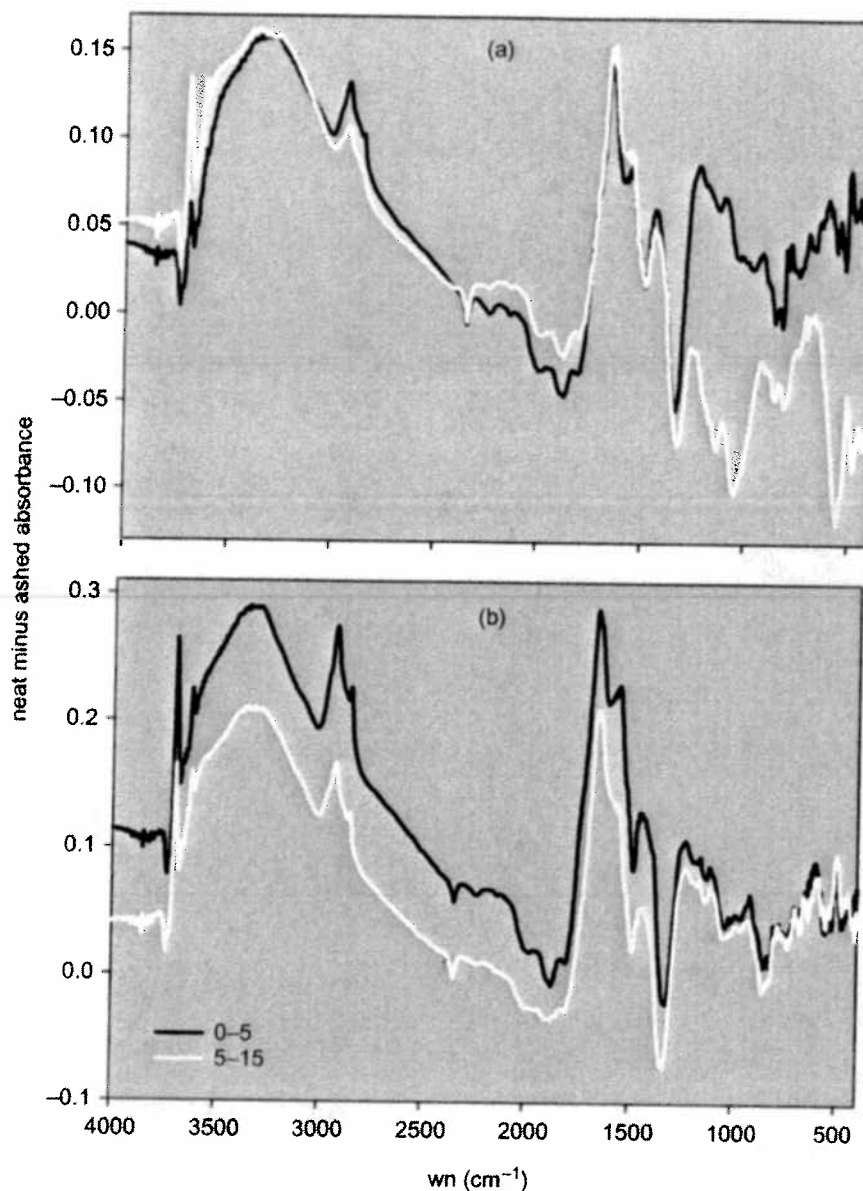


Figure 2. Subtracted spectra (neat minus ashed) from the WF-NT (a) and prairie (b) of the alternative crop rotations. The 0- to 5-cm and 5- to 15-cm depths are shown.

dominated by organic absorbance in soil spectra. Figure 1 shows that casein, starch, and humic acid all absorb in this band, and this region correlates with total C and N in this set of soils. The sharp protein/humic acid peak at 1650 cm^{-1} , also a mostly organic band according to the subtraction approach, is present in casein (Figure 1) and tends to correlate with soil microbial biomass.

The WF-NT subtracted spectra from 0- to 5-cm and 5- to 15-cm depths follow a very similar pattern from 4000 to 1320 cm^{-1} (Figure 2a). However, the two depths have different subtracted spectral patterns from 1320 to 400 cm^{-1} , with the lower depth having more mineral absorbance in this region compared to the surface layer. Figure 1 shows that silica and bentonite clay have several spectral features in this region at 1100 , 800 , and 650 cm^{-1} , although the organic standards also show some features in this range. Figure 2a shows

that 1330 cm^{-1} is possibly a band dominated by mineral absorption and forms a negative feature in the 5- to 15-cm depth subtracted spectrum of the WF-NT. This band forms a shoulder on a peak at 1260 cm^{-1} on pure clay spectra (Figure 1).

Similar to the WF-NT, the subtracted spectra of the prairie soil have the greatest values at the broad 3400 cm^{-1} OH/NH band, the $2870\text{--}2950\text{ cm}^{-1}$ aliphatic CH band, and the $1700\text{--}1550\text{ cm}^{-1}$ region (Figure 2b), with the shallow samples having greater subtracted absorbance from 1000 to 4000 cm^{-1} . The carboxylic OH band at 2600 cm^{-1} , the protein peak at 1554 , the C-O peak at 1442 cm^{-1} , and the aromatic peak at 1230 cm^{-1} are all greater in the prairie shallow soils subtracted spectra. Absorbance at $1650\text{--}1660$ and 1556 cm^{-1} (amides, humic acid), 1581 cm^{-1} (C=C in black carbon), and $2870\text{--}2950\text{ cm}^{-1}$ (alkyl CH_2) have all been found to be important in mid-IR calibrations for soil C in a different set of soils (Janik et al. 2007). Our subtraction data suggest that these bands may have wider applications for marking the presence of high organic matter in a wider variety of samples. On the contrary, Janik et al. (2007) found that bands between 1400 and 1000 cm^{-1} putatively explained by alkyl CH_2 , aromatic CH, and carbohydrate have high partial least squares regression coefficients for soil C and particulate organic C quantification. We see from our subtraction approach that they may be of mostly mineral origin in lower depths of cultivated soil. It is possible that there is a negative correlation of these bands with soil C. These bands between 1400 and 1000 cm^{-1} vary in their mineral or organic character depending on the soil type, with the greater organic matter and surface soils having more mineral absorption in this region.

The prairie soils differ from the WF-NT in that the region between 1340 and 400 cm^{-1} has very similar values between the 0- to 5-cm and 5- to 15-cm depths, mostly above zero, suggesting that in both depths, absorbance tends to be from organic origin. Tables 2 and 3 shows that the prairie soils have much greater organic content at either depth compared to the rest of the treatments, and this has resulted in a stronger influence of organic material in the absorbance spanning the mid-IR range.

Principal Components Analysis (PCA)

The PCA resolved the prairie samples from the crop rotations and grass plots, with the prairie samples having more negative values along component 3 (Figure 3). The crop rotations, however, did not have different spectral properties among themselves according to PCA. Component 3 loadings indicate that the prairie soils absorb more at the $2950\text{--}2870\text{ cm}^{-1}$ band for aliphatic CH (Haberhauer and Gerzabek 1999; Janik et al. 2007; Sarkhot et al. 2007) and at the aromatic --CH band at 1230 cm^{-1} (Janik et al. 2007) relative to the soils from the crop rotations (Figure 4). These two spectral features point to the greater organic-matter content of the prairie soils (Tables 2 and 3). Note that the 1230 cm^{-1} feature is close and could potentially be masked by clay absorbance at 1260 (as in bentonite). The bands at $2950\text{--}2870\text{ cm}^{-1}$ are also present in starch, humic acid, and casein (Figure 1) and are shown to be of organic origin by our subtraction analysis (Figure 2). Component 3 loadings also indicate that the crop rotation soils as a whole absorb at the $1790\text{--}2000\text{ cm}^{-1}$ quartz overtone region and at the clay OH band at 3600 , underscoring the more mineral nature of the cultivated soils (Figure 4). Note that the grass plots, even with their greater soil C content (Tables 2 and 3), still had more spectral properties, and thus soil C quality, similar to the crop rotation soils.

The same PCA as in Figure 3, this time coded by depth (Figure 5), shows a depth effect, with the 0- to 5-cm samples having lower scores than the 5- to 15-cm samples along component 2. Component 2 loadings indicate that the 0- to 5-cm soils absorb more than the 5- to 15-cm soils at a broad region between 1270 and 1460 cm^{-1} (Figure 6). The peak

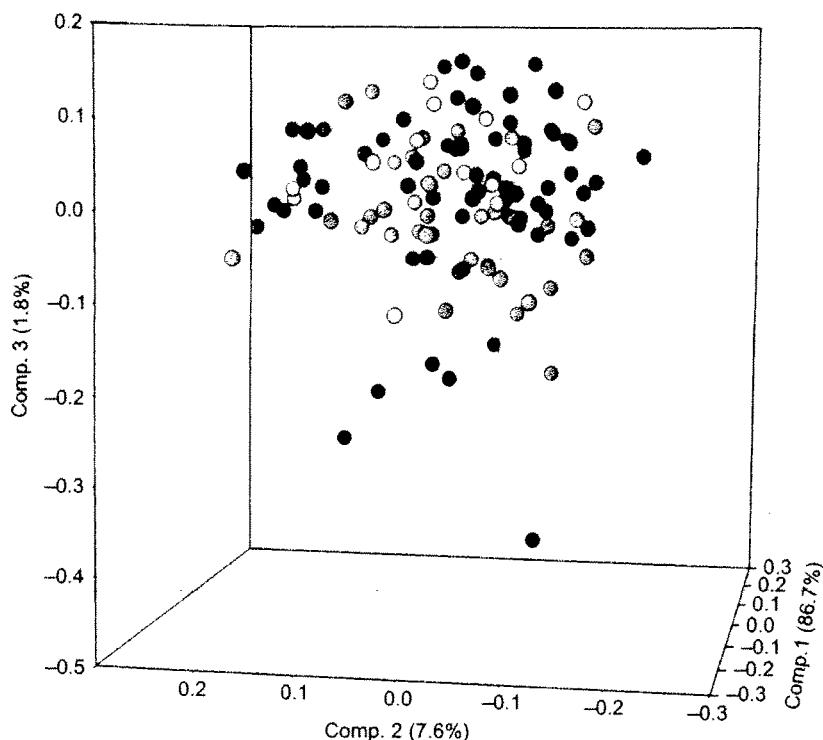


Figure 3. Principal components analysis of the midinfrared diffuse reflectance spectra of prairie soils (red), grass (green), corn–wheat–fallow (pink), corn–millet–fallow–wheat (grey), corn–millet–pea–wheat (maroon), corn–millet–wheat (light blue), fallow–wheat conventional till (yellow), and fallow–wheat no till (blue). Both depths are included in the PCA. The percentage of the total spectral variance accounted for by each component is in parentheses (color figure available online).

at 1352 cm^{-1} is possibly due to organic absorption because this band forms a shoulder on humic acid and starch spectra (Figure 1), and it is in the region of CH absorption in aliphatics, as well as phenolic, or COO stretching vibrations in oxidized black carbon (Janik et al. 2007). The 0- to 5-cm soils also absorb at the carboxylic acid/ester band at 1730 cm^{-1} , which is important for soil organic C determinations (Janik et al. 2007). Our results show that these ester bands represent labile soil C and thus decrease with depth. However, Cox et al. (2000) state that this band is also characteristic of soil humic compounds. Loadings show that the 0- to 5-cm soils also absorb at 1055 cm^{-1} , which is a polysaccharide band, although it could also be assigned to Si–O vibrations in clay. This band is also important for soil organic C calibrations (Janik et al. 2007). Sarkhot et al. (2007) found this band in soil aggregates, indicating the presence of polysaccharide binding agent. The shallow depth also absorbs at 816 and 562 cm^{-1} relative to the 5- to 15-cm depth. The 816 cm^{-1} band is prominent in silica (Figure 1), but spectral subtraction shows that the 562 cm^{-1} band can be of mineral or organic origin depending on the sampling depth. The 5- to 15-cm spectra, in turn, are characterized by greater absorbance at the 3620 cm^{-1} clay hydroxyl band according to PCA loadings (Figure 6).

Correlation Analysis of Spectral Data and Analytes

We determined the correlation coefficient (R) to find out if absorbance at specific mid-IR bands can denote soil quality indicators. The spectral data were correlated against soil

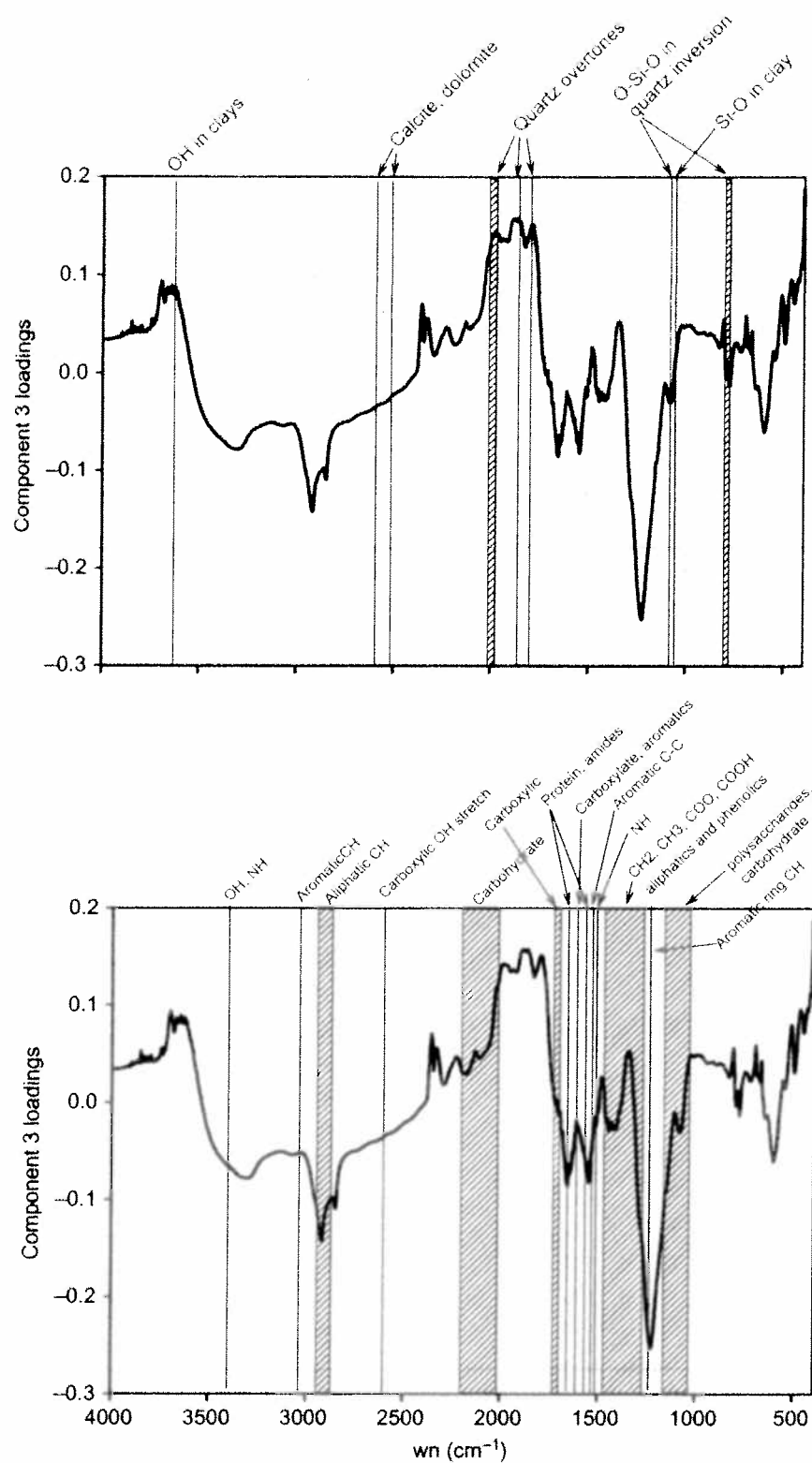


Figure 4. Component 3 loadings for the PCA shown in Figure 3. The top graph is coded according to mineral spectral bands, and the bottom graph is coded according to organic bands.

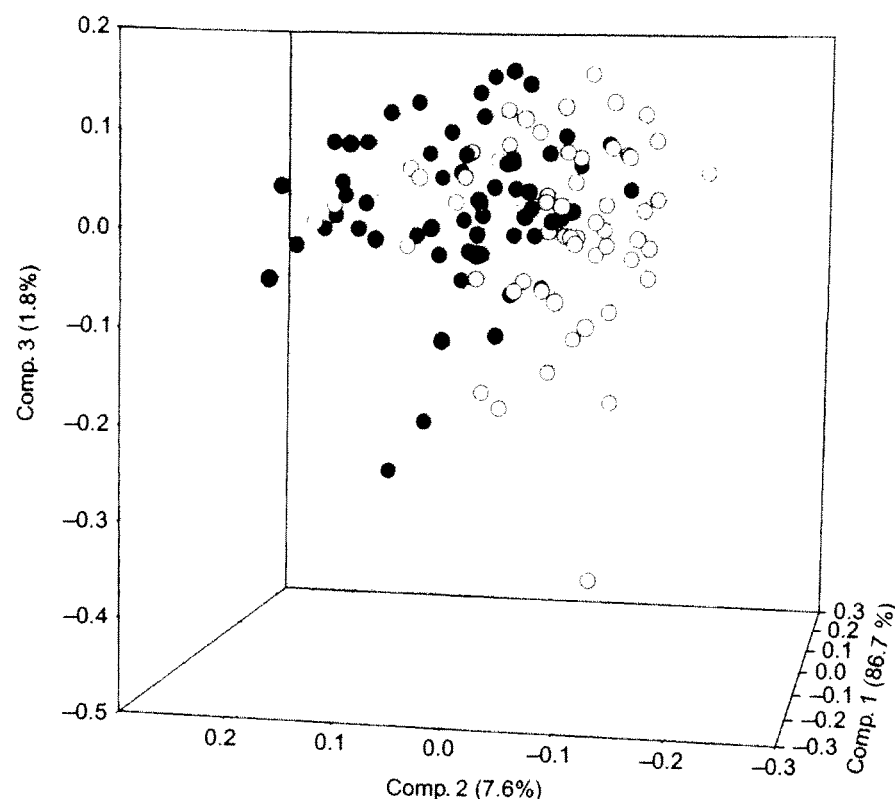


Figure 5. Principal components analysis of the midinfrared diffuse reflectance spectra of 0- to 5-cm-deep (white) and 5- to 15-cm-deep (black) soil samples obtained in 2005. The percentage of the total spectral variance accounted for by each component is in parentheses.

C (as percentages), soil N, bulk density, and microbial biomass C and N. We used the whole set of soils (both depths together). Only total soil C and N achieved correlation R scores greater than 0.5, and both analytes followed a very similar pattern of R scores (Figure 7). The greatest absolute R values for total C were at 3700 cm^{-1} ($R = -0.58$), 2920 cm^{-1} ($R = 0.43$), and 1830 cm^{-1} ($R = -0.43$). Correlation with 2920 cm^{-1} indicates a close relationship of soil C with aliphatic CH stretching absorbance (Haberhauer and Gerzabek 1999; Janik et al. 2007; Sarkhot et al. 2007), a band characteristic of the prairie soils as indicated by PCA. Absorbance at 1830 cm^{-1} is due to quartz overtone combination bands (Nguyen, Janik, and Raupach 1991). The negative correlation between soil C and 1830 cm^{-1} suggests that soil C and N decline with soil quartz content. Correlation at 3700 cm^{-1} indicates that clay hydroxyl stretching absorbance is negatively correlated with soil C and N (Nguyen, Janik, and Raupach 1991). In contrast, Burke et al. (1989) found that in a large set of Central Plains grassland soils, organic C and soil clay contents had a strong relationship according to regression analysis. A correlation analysis of the 0- to 5-cm depth exclusively also shows the clay band as having a high negative correlation to soil C (data not shown), so the relationship between the spectral clay band and soil C and N is not an artifact of having clay or soil C differences between depths. Soil bulk density has a correlation pattern that is generally opposite to that of the total C and N. In this study, we show that the prairie system has significantly less bulk density than the crop rotation treatments, while at the same time having the greatest total soil C and N (Tables 2 and 3), which may help explain the inverse relationship between the soil C and bulk density.

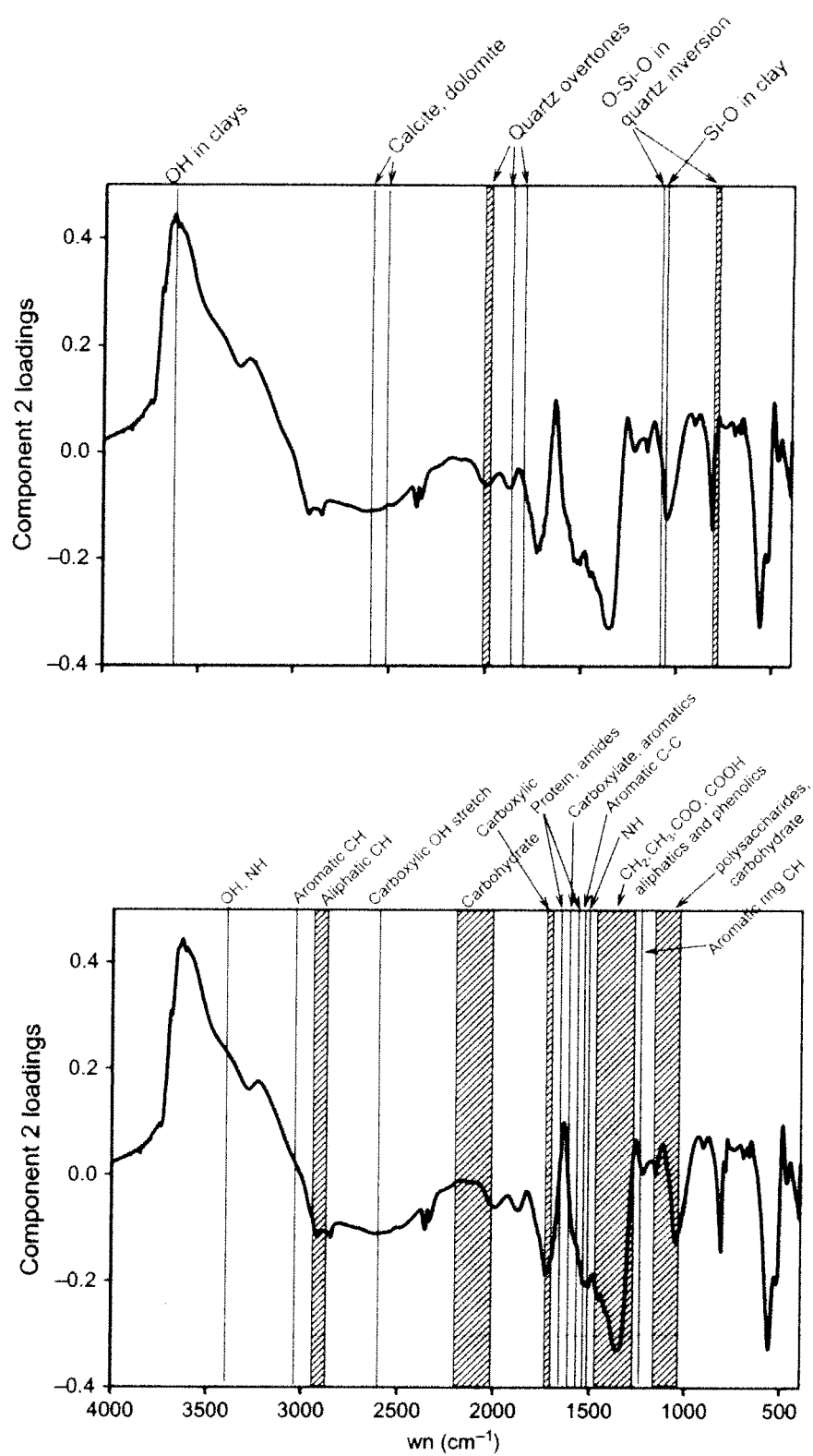


Figure 6. Component 2 loadings for the PCA shown in Figure 5. The top graph is coded according to mineral spectral bands, and the bottom graph is coded according to organic bands.

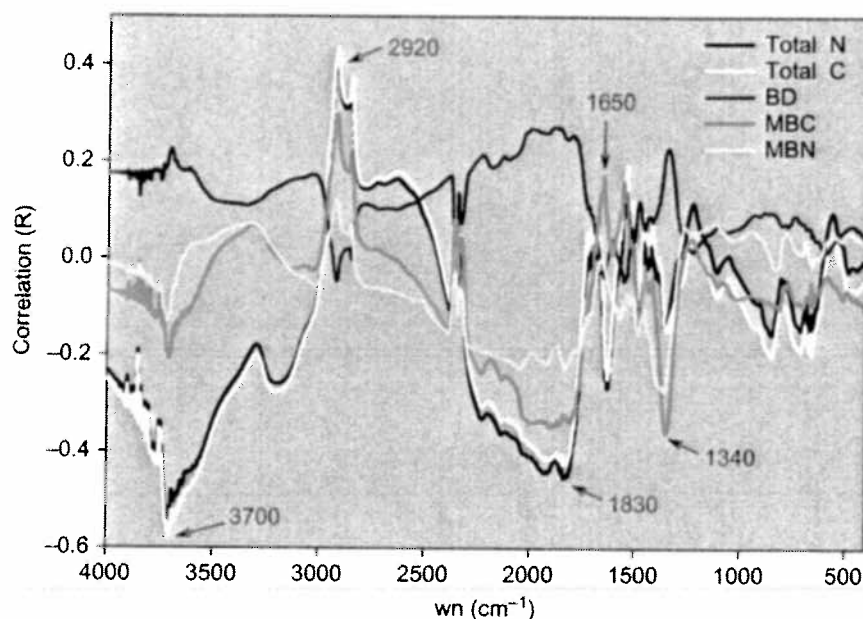


Figure 7. Correlation scores between midinfrared spectral data and soil analytes for the alternative crop rotations soils. BD is bulk density, MBC is microbial biomass C, and MBN is microbial biomass N; $n = 120$ (color figure available online).

The correlation of MBC with the spectral data follows a similar pattern to that of the soil total N and C (Figure 7). However, the MBC R scores differ from those of soil C at 1650 and 1340 cm^{-1} . Casein shows the protein band at 1650 cm^{-1} , while humic acid has strong absorbance near 1340 cm^{-1} (Figure 1). We hypothesize that the band at 1340 cm^{-1} represents stable soil C not readily utilized by microbes to produce MBC. The greater correlation of microbial biomass with absorbance at 1650 cm^{-1} indicates a response in absorbance due to microbial proteins. The stronger R score of soil C at 1340 cm^{-1} indicates a stronger absorbance of the soil C than the microbial material due to phenolic or COO stretching vibrations in the more oxidized soil C.

Conclusions

We have shown that the mid-IR can be a very informational technique that can help indicate important soil quality parameters in these sites from the central Great Plains. The PCA analysis can distinguish the better quality prairie soils from the cultivated soils with their depleted nutrient pools and microbial quality. This study shows that absorbances at 2950–2870 cm^{-1} and 1230 cm^{-1} are associated with the high-quality prairie soil C. After 15 years, the grassland treatment is increasing in C quantity, but the C chemistry as measured by IR spectroscopy is still not like the better quality prairie soils.

References

- Acosta Martinez, V., M. M. Mikha, and M. F. Vigil. 2007. Microbial communities and enzyme activities in soils under alternative crop rotations compared to wheat-fallow for the central Great Plains. *Applied Soil Ecology* 37:41–52.

- Anderson, R. L., R. A. Bowman, D. C. Nielsen, M. F. Vigil, R. M. Aiken, and J. G. Benjamin. 1999. Alternative crop rotations for the central Great Plains. *Journal of Production Agriculture* 12:95–99.
- Baes, A. U., and P. R. Bloom. 1989. Diffuse reflectance and transmission Fourier transform infrared (DRIFT) spectroscopy of humic and fulvic acids. *Soil Science Society of America Journal* 53:695–700.
- Bauer, A., and A. L. Black. 1981. Soil carbon, nitrogen, and bulk density comparisons in two cropland tillage systems after 25 years and in virgin grassland. *Soil Science Society of America Journal* 45:1166–1170.
- Benjamin, J. G., M. M. Mikha, and M. F. Vigil. 2008. Organic carbon effects on soil physical and hydraulic properties in a semi-arid climate. *Soil Science Society of America Journal* 72:1357–1362.
- Bowman, R. A., M. F. Vigil, D. C. Nielsen, and R. L. Anderson. 1999. Soil organic matter changes in intensively cropped dryland systems. *Soil Science Society of America Journal* 63:186–191.
- Burke, I. C., C. M. Yonker, W. J. Parton, C. V. Cole, K. Flach, and D. S. Schimel. 1989. Texture, climate, and cultivation effects on soil organic matter content in U.S. grassland soils. *Soil Science Society of America Journal* 53:800–805.
- Calderón, F. J., J. B. Reeves III, H. P. Collins, and E. A. Paul. 2011. Chemical differences in soil organic matter fractions determined by diffuse reflectance mid-infrared spectroscopy. *Soil Science Society of America Journal* 75:568–579.
- Cox, R., H. L. Peterson, J. Young, C. Cusik, and E. O. Espinoza. 2000. The forensic analysis of soil organic by FTIR. *Forensic Science International* 108 (2): 107–116.
- Haberhauer, G., and M. H. Gerzabek. 1999. Drift and transmission FT-IR spectroscopy of forest soils: An approach to determine decomposition processes of forest litter. *Vibrational Spectroscopy* 19:413–417.
- Janik, L. J., J. Skjemstad, K. Shepherd, and L. Spouncer. 2007. The prediction of soil carbon fractions using mid-infrared-partial least square analysis. *Australian Journal of Soil Research* 45 (2): 73–81.
- Madejová, J. 2003. FTIR techniques in clay mineral studies. *Vibrational Spectroscopy* 31:1–10.
- McCarty, G. W., and J. B. Reeves III. 2000. Development of rapid instrumental methods for measuring soil organic carbon. In *Assessment methods for soil carbon*, ed. R. Lal et al., 371–380. Boca Raton, FL: Lewis Publishers.
- McCarty, G. W., J. B. Reeves III, V. B. Reeves, R. F. Follett, and J. M. Kimble. 2002. Mid-infrared and near-infrared diffuse reflectance spectroscopy for soil carbon measurement. *Soil Science Society of America Journal* 66:640–646.
- Mikha, M. M., M. F. Vigil, M. A. Liebig, R. A. Bowman, B. McConkey, E. Deibert, and J. L. Pikul Jr. 2006. Cropping system influences on soil chemical properties and soil quality in the Great Plains. *Renewable Agriculture and Food Systems* 21(1): 26–35.
- Nguyen, T., L. J. Janik, and M. Raupach. 1991. Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy in soil studies. *Australian Journal of Soil Research* 29 (1): 49–67.
- Peterson, G. A., A. D. Halvorson, J. L. Havlin, O. R. Jones, D. J. Lyon, and D. L. Tanaka. 1998. Reduced tillage and increasing cropping intensity in the Great Plains conserves soil C. *Soil Tillage and Research* 47:207–218.
- Reeves III, J. B., G. W. McCarty, and V. B. Reeves. 2001. Mid-infrared diffuse reflectance spectroscopy for the quantitative analysis of agricultural soils. *Journal of Agriculture and Food Chemistry* 49:766–772.
- Reicosky, D., W. Kemper, G. Langdale, C. Douglas, and P. Rasmussen. 1995. Soil organic matter changes resulting from tillage. *Journal of Soil and Water Conservation* 50:253–261.
- Sarkhot, D. V., N. B. Comerford, E. J. Jokela, J. B. Reeves III, and W. Harris. 2007. Aggregation and aggregate carbon in a forested southeastern coastal plain Spodosol. *Soil Science Society of America Journal* 71:1779–1787.

- Shirshova, L. T., E. A. Ghabbour, and G. Davies. 2006. Spectroscopic characterization of humic acid fractions isolated from soil using different extraction procedures. *Geoderma* 133:204–216.
- Smika, D. E. 1970. Summer fallow for dryland winter wheat in the semiarid Great Plains. *Agronomy Journal* 62:15.
- Smika, D. E. 1983. Cropping practices: Introduction. In *Dryland agriculture*, ed. H. E. Dregne and W. O. Willis, 293–295. Madison, Wisc.: ASA, CSSA, SSSA.